Journal of the Royal Society of Western Australia, 72 (4), 1990, 95-108

Natural products from Western Australian marine organisms

E L Ghisalberti & P R Jefferies

Department of Organic Chemistry, The University of Western Australia
Nedlands WA 6009, Australia

Manuscript received January 1989; accepted June 1989

Abstract

The natural products isolated from marine organisms found in Western Australia are reviewed. Although over 110 different compounds have been identified these result from only a preliminary survey of sponges, a few examples of other marine fauna, algae and sea grasses. The discussion takes a chemotaxonomic approach highlighting the sources of the metabolites and the uniqueness or otherwise of the metabolites occuring in organisms available in Western Australia. The biological activity of some of these metabolites is noted. In the Appendix the structures of all compounds identified are presented together with the source organism and, where the information is available, the proportion of each metabolite of the dry weight of the organism. The information contained in this review should serve as a starting point and a stimulus for more detailed studies of the biology, chemistry and ecology of the Western Australian marine environment.

Introduction

Marine natural products chemistry has experienced a rapid growth in recent years. Organic chemists have recognized that the seas and oceans, which contain an estimated 500 000 species of plants, animals and microbes, are a major source of new natural products and their study is being vigorously pursued. In Australia research in marine natural products received little consideration before 1960. (For a summary of the early interest by biologists in Australian marine natural products research see Baker 1976).

Studies into the chemistry of Australian marine organisms began in Queensland in the late 1950s with Sutherland, who was mainly involved in the isolation and identification of quinonoid pigments from the crinoids of the Great Barrier Reef. The accessibility of diverse marine life of the Great Barrier Reef to a number of Australian research institutions together with the advent of more efficient collection procedures (*ie* SCUBA) made research into marine natural products feasible in those centres. The Roche Research Institute of Marine Pharmacology (RRIMP) during its period of operation (April 1974 - June 1981) undertook a systematic examination of numerous marine organisms from the eastern Australian coast in a search for commercially viable biologically active compounds (Wells 1979). However little information is available from this source on the marine natural products from the coastal waters of Western Australia. This coastline, bounded to the south by the cold waters of the Southern Ocean, extends to subtropical and tropical waters in the north. The coastal topography includes extensive limestone cliffs, rocky and sandy beaches, coral reefs and mangrove communities. Many of these differing environments may harbour new and indigenous species of flora and fauna, some perhaps possessing novel chemistry.

In embarking on an investigation of the natural products from marine organisms of the Western Australian coast we chose to limit ourselves to the Porifera and Marine Algae, which have proved prolific sources of natural products elsewhere. During the preliminary period of this investigation collections were restricted to shore based 'dives' (SCUBA and snorkel) and 'beachwash', along the coast from Augusta to Lancelin, together with several trips to reefs off Perth. With the availability of the marine research vessel 'Uniwest' to the University of Western Australia the potential for more ambitious collections was realized. An expedition to the Abrolhos Islands in May 1981 provided many interesting specimens as well as a valuable test for 'onboard' procedures.

This paper presents a review of the natural products chemistry of Western Australian marine organisms collected by us and includes work carried out by other groups which have published work on the topic. We hope that this review, which essentially is an inventory of organic chemicals available in Western Australian waters, will provide a starting point and stimulus for further study of the biology and chemistry of Western Australian marine environments. Note that in the text numbers in bold face refer to compounds whose structural formulae are presented in numerical order in the Appendix.

A70617-1

Porifera

Marine fauna of the phylum Porifera, sponges, are difficult to classify taxonomically as many of their morphological features differ with environmental as well as genetic variations. Even chemotaxonomic observations require careful interpretation since sponges can exist in symbiosis with blue-green algae and bacteria, yielding natural products with uncertain biogenetic origins (Berquist & Wells 1983). Table 1 is a list of sponges collected in Western Australia which have been investigated for secondary metabolites.

Sponges are classified into one of four classes, Calcarea, Hexactinellida, Sclerospongiae or Demospongiae, based on the chemical and structural nature of their skeletal material (Bergquist 1978). The Demospongiae constitutes the most diverse and ecologically significant group and information on this class has dominated the literature on sponge natural products. The majority of Australian Demospongiae examined for interesting secondary metabolites are members of the order Dictyoceratida, in which the inorganic sponge skeleton of the other orders is replaced by an organic fibrous network. Sponges of this order can be grouped into three families, Dysideidae, Spongiidae and Thorectidae (Bergquist 1978). The Dysideidae is a small family containing only one large genus, *Dysidea*. Two members of this family, *Dysidea* and an undetermined genus, have been collected off the West Australian coast and examined chemically (Capon 1982, Dunlop, Ghisalberti & Jefferies, unpublished results). Both were found to produce examples of furanosesquiterpenes, (**1-4**) and (**1,2**) respectively, previously isolated from *Dysidea* species, *eg D. herbacea*, from the Great Barrier Reef. *Dysidea* species provide a number of different sesquiterpenoid skeletons and have proved consistent in producing this type of terpenoid metabolite. The presence in some *Dysidea* of non-terpenoid halogenated metabolites has been ascribed to involvement of extraneous microorganisms, particularly cyanophytes (Bergquist & Wells 1983).

From the Spongiidae family samples of several genera, *Phyllospongia, Spongia, Leiosella, Lendenfeldia* and an undetermined genus have been studied. Specimens of a *Phyllospongia* sp collected off Burns Beach and of an undetermined genus of the Spongiidae did not yield any recognisable metabolites. In common with other Australian *Spongia* species the specimen from Western Australia contained a C_{21} difuranoterpene (**5**) (Capon *et al* 1982a) Although **5** is a new compound it is related to other dominant *Spongia* metabolites. The *Leiosella* sp investigated also contained similar terpenes (**6,7**) (Capon *et al* 1982a) previously isolated from *Spongia* species from New South Wales and Victoria. In addition to the two C_{21} furanoterpenes (**8,9**) a *Lendenfeldia* sp also produces a set of cyclic sesterterpenes (**10-14**) (Kazlauskas *et al* 1982b). This places *Lendenfeldia* taxonomically closer to *Carteriospongia* and makes these two genera distinct from *Spongia*. *Spongia* represents a point of close similarity to genera within the Thorectidae, which with 14 genera is the largest family of the Dictyoceratida and morphologically the most diverse.

Several collections of *Ircinia* from Shark Bay were shown to contain the linear sesterterpene tetronic acids (**15,16**) and minor amounts of a mixture of sterol epidioxides (**17-19**) (Cassidy 1982). On the other hand an *Ircinia* sp from Rottnest yielded squalene (**20**), furospinosulin (**21**), the logical precursor of the tetronic acid (**15**), as well as the

Table 1

Western Australian Sponges (Class: Demospongiae) mentioned in this review

Sub-Class	Order	Family	Genus	Collection site	Specimen number
Ceractinomorpha	Dictyoceratida	Dysideidae	undet. genus*	Gun Island, Houtman Abrolhos	WAM 430-81
			Dysidea	Lefebre Island	SB 036
		Spongiidae	*Lendenfeldia*	Quobba Lagoon	
			Spongia	Gun Island, Houtman Albrolhos	WAM 429-81
			Leiosella	Rottnest Island	WAM 83-82
			undet. genus	Lancelin	WAM 147-82
			Phyllospongia	Burns Beach	WAM 403-80
		Thorectidae	*Ircinia*	Wooramel Delta	WAM 44-82
					WAM 148-82
					WAM 149-82
				Mewstone, Rottnest	WAM 16-82
			Thorectandra	Carnac Island	WAM 84-82
	Poecilosclerida	Clathriidae	*Clathria*	Carnac Island	WAM 51-82
		Desmacidonidae	*Desmacidon*	Carnac Island	WAM 53-82
	Haplosclerida	Haliclonidae	*Haliclona*	Cosy Corner, Hamelin Bay	WAM 425-81
		Adociidae	*Adocia*	Carnac Island	WAM 17-82
		Callyspongiidae	new genus	Cosy Corner, Hamelin Bay	WAM 17-82
			undet. genus	Rottnest Island	WAM 431-81
			Dactylia	Carnac Island	WAM 47-82
				Rottnest Island	WAM 14-82
	Halichondrida	Halichondriidae	*Halichondria*	40 km west Lancelin	WAM 14-82
	Verongida	Verongidae	*Iotrochota*	Five Fathom Bank, Fremantle	
Tetractinomorpha	Choristida	Jaspidae	*Jaspis*	Carnac Island	WAM 54-82
	Hadromerida	Suberitidae	*Suberites*	Carnac Island	WAM 52-82
		Spirastrellidae	*Spirastrella*	Carnac Island	WAM 49-82
	Axinellida	Desmoxyiidae	*Higginsia*	40 km west Lancelin	WAM 145-82
	Dendroceratida	Aplysillidae	*Chelonaplysilla*	Carnac Island	WAM 48-82

* Classification is doubtful
† Specimens with WAM prefix have been lodged with the Western Australian Museum

analogues (**22**) and (**23**) (Capon 1982). A *Thorectandra* sp yielded **21** and the indole salt (**24**) derivative of aplysinopsin (Capon 1982) previously isolated from other Australian *Thorectandra* species and *Fascaplysinopsis reticulata*, which has many features in common with *Thorectandra*.

Two samples of the order Poecilosclerida, *Clathria* (Family: Clathriidae) and *Desmacidon* (Family: Desmacidonidae) have been collected. Preliminary analysis failed to reveal distinct metabolites.

A *Haliclona* sp (Order: Haplosclerida; Family: Haliclonidae) collected at Hamelin Bay contained two new cyclic ethers (**25,26**) (Capon *et al* 1982b). The Callyspongiidae are in the same order and were represented in our collection by three genera, *Dactylia* sp, a new genus and an undetermined genus. From the *Dactylia* sp only 4-hydroxybenzaldehyde (**27**) could be identified (Capon 1982). The metabolites of the other two collections were similar (**28-30**) and belong to an unusual group of polyhalogenated biphenyl ethers (Capon 1982, Capon *et al* 1981c). This group of metabolites have also been found in *Dysidea herbacea*. *D. chlorea* and *Carteriospongia foliascens*. These results when taken together are of interest particularly if one notes that many *Casteriospongia* species are known to contain high levels of blue-green algae within their matrix. It seems that these metabolites could arise from the algae or from a combination of algal-sponge metabolism.

Three new sesquiterpenes (**31-33**) and (-)-β-bisabolene (**34**) were isolated from the only specimen of the order Halichondrida, *Halichondria* sp, collected (Capon *et al* 1982c). The sesquiterpenes accounted for 11.2% of the dry biomass. A brominated indole derivative (**35**) was the major metabolite isolated from *Iotrochota* sp, a member of the Verongida family (Dellar *et al* 1981). Specimens of *Jaspis*, *Suberites* and *Spirastrella* were also collected and analysed but did not yield distinct metabolites. The last sponge to be considered is a *Higginsia* sp (family: Desmoxyiidae). Since its classification in 1945 there appear to have been only a small number of collections of this genus including the detection of spicules of *Higginsia* sp in the gut of nudibranchs (Thompson *et al* 1982). The WA specimen yielded a mixture of four novel diterpenes (**36-39**) (Cassidy *et al* 1985).

Other marine fauna

For the sake of completeness mention should be made of isolated studies on other WA marine fauna. From a compound ascidian collected in the Abrolhos, the blue pigment (**40**) was isolated (Kazlauskas *et al* 1982a).

Echinodermata are abundant in Western Australian waters and they are collected adventitiously in large numbers in the nets of prawn trawlers operating in Shark Bay. Many species are brilliantly coloured and their ready availability made them suitable organisms for a marine natural products study.

There are five classes of echinoderms: Asteroidea (starfish), Ophiuroidea (brittle star), Echinoidea (sea urchin), Holothuroidea (sea cucumber) and Crinoidea (feather star). All five classes contain carotenoids which may be either "carotenes" or "xanthophylls". In the asteroids, alcoholic xanthophylls are often bound to integumentary proteins, differences between which probably account for the wide variations in colours often observed among different specimens of the same species (Grossert 1972). Sixteen species of echinoderms (Table 2) collected from Western Australian waters were examined for the presence of pigments and terpenoids. Terpenes were not detected. Eleven of these, within the class Holothuroidea (one), Ophiuroidea (six), Echinoidea (three) and Asteroidea (one) contained either no extractable pigment or very little. Three of the five remaining species (Crinoidea) were rich in pigments. *Comantheria briareus* yielded the linear naphthopyrones (**41-43**) and the angular naphthopyrone (**44**). *Comathula solaris* afforded the anthraquinones (**45,46**) and *C. rotolaria* yielded (**46,47**) (Francesconi 1980, 1983).

Table 2

List of Echinoderms investigated for presence of pigments and terpenes

Class	Family	Species
Holothuroidea	Cucumariidae	*Pentacta crassa* (Ekman)
Ophiuroidea	Euryalidae	*Euryale aspera* (Lamarck)
	Gorgonocephalidae	*Astroboa granulatus* (H L Clark)
		Astroboa nuda (Lyman)
	Ophiotrichidae	*Ophiothrix ciliaris* (Lamarck)
		Ophiothrix (Acanthophiothrix) aff. *purpurea* (von Martens)
		Ophiomaza cacaotica (Lyman)
Echinoidea	Temnopleuridae	*Holopneustes porosissimus*
		Salmacis virgulata
	Citaridae	*Prionocidaris bispinosa* (Lamarck)
Crinoidea	Comasteridae	*Comatula rotalaria* (Lamarck)
		Comatula solaris (Lamarck)
		Comantheria briareus (Bell)
		Comanthina belli (P H Carpenter)
	Himerometridae	*Amphimetra tessellata* (J Muller)
Asteroidea	Metrodiridae	*Metrodira subulata* (Gray)

Arsenobetaine (**48**) has been isolated from the tail muscle of the western rock lobster (*Panulirus cygnus*) (Cannon *et al* 1981), from the flesh of the dusky shark (*Carcharinus obscurus*) (Cannon *et al* 1981), both of which are commercially important seafoods, and in the flesh of the school whiting (*Sillago bassensis*) (Edmonds & Francesconi 1981a). The arsenic containing ribofuranosides (**49,50**) have been isolated from the kidney of the giant clam, *Tridacna maxima* taken from Shark Bay (Edmonds & Francesconi 1982). It has been suggested that these compounds are metabolic waste products of the zooxanthellae present in clam tissue and that their biosynthesis is a general response of algae to oceanic arsenate.

Algae

The marine algae consist of those structurally simple marine plants without roots, stems or leaves and having primitive methods of reproduction. Commonly known as seaweeds they may be of macroscopic or microscopic form and collectively are the basis of all marine food chains. Macroalgae, the subject of our investigations, fall into three divisions: Chlorophyta (green), Phaeophyta (brown) and Rhodophyta (red). The Cyanophyta (blue-green) which are procaryotic, constitute a less accessible, but none the less important, fourth division (Price 1981).

Unlike the Porifera it is possible to classify taxonomically many algae to at least the genus level 'in the field' based on their macroscopic characteristics. Although 'colour coded' into divisions, colour is sometimes not a reliable guide, Rhodophyta growing in intertidal zones often appear brownish or even yellow rather than red. Classification to the species level sometimes requires detailed microscopic examinations. Table 3 lists Western Australian algae which have been studied as sources of natural products.

The Chlorophyta are distinguished from other algae by the presence of chlorophyll b in the pigment complex, the synthesis and storage of starch as the predominant reserve material and motile cells (McRaild 1981). Of the little published data on the natural products from Australian Chlorophyta most is concerned with the genus *Caulerpa*, which is widely distributed in tropical and temperate Australian waters. Several species of *Caulerpa* were collected from Western Australian waters and examined for metabolites and two distinct groups were identified. *C. flexilis* var *muelleri* and *C. trifaria* produced the sesquiterpenes (**51,52**) and the diterpene (**53**) respectively (Capon *et al* 1981a, Capon *et al* 1983). These compounds were new but are biogenetically related to compounds previously isolated from *C. brownii*, *C.flexilis* and *C. trifaria* from the eastern seaboard (Wells 1979). Samples of *C. brownii*, *C. flexilis*, *C. peltata* and *C. racemosa* collected at different points along the WA coast did not yield terpenoid metabolites and the last two contained the pigment caulerpin (**54**) (Capon *et al* 1983). Such observations are not uncommon in marine natural products chemistry and can be explained by considering variations in environment *ie* stress or geographical variants with differing secondary metabolism but similar morphological structure.

Unlike the Chlorophyta which can be found in both marine and freshwater environments the Phaeophyta are almost entirely marine (Clayton 1981). Ranging in size from thin crusts to massive kelps the brown algae are the most conspicuous seaweeds of rocky temperature shores making them an obvious source of material for the marine natural products chemist. Of more than 100 genera of brown algae recorded from the shores and subtidal regions of Australia and New Zealand about one quarter are endemic (Clayton 1981).

Two samples of the order Fucales, family Cystoseiraceae, have been examined. An unclassified *Cystophora* sp yielded the carotenoids, β-carotene (**55**) and fucoxanthin (**56**), the phytosterol fucosterol (**57**) and three new derivatives (**58-60**) of geranyl toluquinol (Capon *et al* 1981b). *Caulocystis uvifera* produces the antiinflammatory salicylic acid (**61**) the linear alkene (**62**) and ketones (**63-65**), and qualitatively is similar to *C. cephalornithos* (Capon 1982). A *Sargassum* sp (family: Sargassaceae) contained the prenylated derivatives of toluquinol (**66,67**) (Arrowsmith 1983).

Table 3

Western Australian Algae examined for secondary metabolites*

Division	Class	Order	Family	Genus	Collection site
Chlorophyta	Chlorophyceae	Caulerpales	Caulerpaceae	*Caulerpa brownii* Endlicher	Augusta to Lancelin
				Caulerpa flexilis (Lamx.) var. *muelleri* (Sond.)Wom.	Cosy Corner
				Caulerpa peltata Lamouroux	Big Nook, Houtman Abrolhos
				Caulerpa racemosa (Forssk.)J.Ag.	Augusta to Lancelin
				Caulerpa trifaria Harvey	Point Peron
Phaeophyta	Phaeophyceae	Fucales	Cystoseriraceae	*Cystophora* sp	Hamelin Bay
				Caulocystis uvifera (C.Ag.)J.Ag.	Wreck Point
			Sargassaceae	*Sargassum* sp	Big Rat Island Lagoon
		Dictyotales	Dictyotaceae	*Dictyota furcellata* (C.Ag.)J.Ag.	Cape Peron, Shark Bay
				Glossophora sp	Big Rat Island Lagoon
		Laminariales	Alariaceae	*Ecklonia radiata* (Turn.)J.Ag.[a]	Whitford Beach
Rhodophyta	Rhodophyceae (subclass Florideae)	Ceramiales	Rhodomelaceae	*Laurencia filiformis* (C.Ag.) Montagne	Yanchep
				Laurencia filiformis f *filiformis* Saito & Womersley	Point Peron
				Laurencia filiformis f *heteroclada* (Harvey) Saito & Womersley	Cottesloe; Lancelin; Shoalwater Bay; Hamelin Bay
				Laurencia majuscula (Harvey) Lucas	Woodman Point
				Choudria sp	Rat Island, Houtman Abrolhos
				Vidalia spiralis Lamouroux[b]	Yanchep
		Gigartinales	Plocamiaceae	*Plocamium mertensii* (Grev.) Harvey	Carnac Island; Hamelin Bay; Lancelin
				Plocamium preissianum Sonder	Augusta
				Plocamium sp	Rottnest
				Plocamium sp	Cottesloe
				Plocamium sp	Big Rat Island
			Phacelocarpaceae	*Phacelocarpus labillardieri* (Mertens) J.Ag.	Cosy Corner
			Hypneaceae	*Hypnea* sp[c]	Quobba Lagoon
		Nemalionales	Bonnemaisoniaceae	*Delisea* sp	Redgate Beach, Hamelin Bay

* Specimen samples of the algae, except those marked a, b, c, have been lodged with the Department of Botany, The University of Western Australia.

The order Dictyotales is one of the most distinct of the Phaeophyta and considerable work on the metabolites produced by members of this order has been published. From WA two species have been examined. A *Glossophora* sp yielded the macrocyclic dialdehyde (**68**) (Arrowsmith 1983) and *Dictyota furcellata* the new dolastane diterpene (**69**) (Dunlop *et al* 1989). The cosmopolitan and sub-tropical genus *Dictyota* has been shown to produce a number of biologically active diterpenes based on the dolastane ring system.

The ability of marine algae to accumulate substantial concentration of arsenic has been known for some time. In efforts to determine the source of arsenic in marine fauna from the unpolluted coastal waters of WA, algae were surveyed and the brown kelp, *Ecklonia radiata* (Order: Laminariales; Family: Alariaceae) was found to contain arsenic at a concentration of 10 mg kg^{-1} (wet weight). Further studies revealed that the arsenic was present in the form of the arseno ribofuranosides (**49**, **70**, **71**) (Edmonds & Francesconi 1983). It is possible that these compounds represent a mode of entry for arsenic into the marine food chain and could well be the source of arsenobetaine (**48**) in marine fauna.

The red algae, Rhodophyta, have many delicate and intricate species. Australasia, with at least 1 100 species and 370 genera, contains a greater diversity of red algae than any other comparably sized region on earth (Kraft & Woelkerling 1981). Chemical studies have revealed them to be a rich source of halogenated terpenes and acetogenins. Particularly prolific in yielding interesting secondary metabolites are the genera *Laurencia* and *Plocamium*.

Laurencia (Order: Ceramiales; Family: Rhodomelaceae) is a common genus on southern Australian coasts and includes numerous species which are often ecologically important (Saito and Womersley 1974). Most species are clearly defined but *L. filiformis* includes three main forms, which have been named *filiformis*, *heteroclada* and *dendritica*, with intergrades between them, and intergrades from it to the related species *L. arbuscula* and *L. tasmanica*. From *L. filiformis* f. *filiformis* we have isolated aplysistatin (**72**) and 6β-hydroxy-aplysistatin (**73**) (Capon *et al* 1981d)

Because of the ecological importance of this genus we have also examined the constituents of samples of *L. filiformis* f. *heteroclada* collected at four different points along the Western Australian coast; Hamelin Bay, Shoalwater Bay (*ca* 50 km south of Perth), Cottesloe Beach (Perth) and Lancelin. In each case the alga was found to elaborate known laurene sesquiterpenes as the major metabolites. Whereas the sample from Hamelin Bay contained only allolaurentirol (**74**), those from Lancelin and Cottesloe Beach in addition produced laurenisol (**75**) and bromolaurenisol (**76**) respectively. In contrast, the Shoalwater Bay sample yielded (**75**), (**76**), isolaurentirol (**77**), filiformin (**78**) and (-)-α-bromocuparene (**79**) (Capon *et al* 1988).

Previous work on two collections of *L. filiformis* f. *heteroclada* from the Eastern States has shown that both contained sesquiterpenes based on the laurene skeleton but in addition one sample contained heterocladol, a halogenated selinane sesquiterpene (Wells 1979). A sample of *L. filiformis* from Lancelin contained compounds (**80**, **81**) based on the selinane skeleton (Brennan & Erickson 1982). These results suggest that the f. *heteroclada*, in terms of the sesquiterpene metabolites it produces, is clearly distinct from the f. *filiformis*. It seems likely that the third form of the *L. filiformis* complex, f. *dendritica*, is also distinct and it is the form which produces prepacifenol, a chamigrene sesquiterpene. In this context it is interesting to note that *L. tasmanica* which can be regarded as an extreme form of the *L. filiformis* complex bordering f. *dendritica* (Saito & Womersley 1974) has been shown to produce a similar compound (Sims *et al* 1973).

In contrast to the *L. filiformis* "complex", *L. majuscula* is a distinctive species widely distributed along the southern Australian coast including Tasmania (Saito & Womersley 1974). *L. majuscula*, collected from Woodmans Point (*ca* 30 km south of Perth), was found to elaborate the known chamigrene sesquiterpenes obtusane (**82**), obtusol (**83**), elatol (**84**) and isoobtusol (**85**). Although these compounds have been isolated from various *Laurencia* species they have not been reported before from *L. majuscula* and differ from the chamigrenes present in the Mediterranean and Japanese varieties (Capon *et al* 1988).

Two other members of the Rhodomelaceae family have been investigated. An undetermined *Chondria* sp, found attached to coral (*Acropora* sp) near Rat Island, in the Eastern Group of Houtman Abrolhos, was observed to rapidly decompose on exposure to air, such that the filamentous alga took on a 'paste' like consistency. In this form the alga was particularly unpleasant to handle, causing a lingering 'tingling' sensation, and emitted a sulphurous odour. Extraction returned a low yield of lipophilic material (0.06%), from which a mono methyl ether of reductic acid (**86**) was recovered (Capon 1982). Reductic acid has been reported as a hydrolysis product of alginic acid (a natural product found in Phaeophyta), L-ascorbic acid and *Laminaria* powder (Aso 1939). Methylation of the product obtained on hydrolysis of the latter afforded a mono methyl ether with the same melting point as **86**. The acidic nature of the decomposed alga (*ca* pH 5) supports speculation that **86** is derived from reductic acid *via* acid catalysed methylation (during extraction with dichloromethane: methanol [1:1], and furthermore that reductic acid is itself a degradation product.

Crude extracts of *Vidalia spiralis* exhibited hypotensive activity. Although the new compound (**87**) was isolated it was not the active principle (Kauzlauskas *et al* 1982c).

The Gigartinales is a large order which is particularly well represented in Australia (*ca* 200 species) (Kraft & Woelhering 1981). The most widely studied genus of this group is *Plocamium* which occurs frequently along the WA coast. A large number of alicyclic and acyclic, brominated and chlorinated, monoterpenes have been isolated from a variety of *Plocamium* spp, collected at geographically distant locations *ie* Antarctica, the British and Californian coasts and the coast of Australia (Capon 1982). On several occasions the same or similar compounds have been reported as constituents of the lipid extract of the digestive gland of sea-hares (*Aplysia* spp), which are known to graze on algae, accumulating toxic secondary metabolites for defensive purposes. The antibacterial properties of *Plocamium* extracts have been known for some time and with the advent of more sophisticated isolation, purification and identification techniques, together with more specific bioassays, it has been possible to identify these unusual, and often unstable, natural products.

During our investigations of local *Plocamium* spp we found that the abundant red alga *P. mertensii*, collected off Perth contained the known rearranged alicyclic monoterpene, plocamadiene-A (**88**), as the only isolatable secondary metabolite (Capon *et al* 1984). At this time, **88** had been reported from a British collection of *P. cartilagineum*, where it was isolated as an oil, and from *P. cartilagineum* collected off the east coast of Australia (Capon 1982). As a result of the latter isolation plocamadiene-A (**88**) was found to possess a novel pharmacological activity "[It] produces a spastic syndrome in mice which persists for several days but is ultimately reversible" (Spence & Wells 1978). The same compound was present in a sample collected at Lancelin together with the related compound (**89**) and the acyclic monoterpene (**90**). A third sample from Hamelin Bay yielded similar compounds (**91-93**) (Bestow 1981). All three samples also contained the glycerylglucose floridoside (**94**).

A collection of *Plocamium preissianum* from Augusta was found to contain a complex mixture of polyhalogenated monoterpenes from which two acyclic compounds **95** and **96** were isolated (as a 1:1 mixture) (Capon 1982). Both **95** and **96** are known metabolites of *P. cartilagineum*, Californian specimens of which were found to elaborate polyhalogenated acyclic monoterpenes whereas British, Spanish and Antarctic speciments yielded alicyclic halogenated monoterpenes (Capon 1982). An unidentified *Plocamium* sp, collected from the beachwash on Rottnest Island, contained the known alicyclic bromotrichloromonoterpene mertensene (**97**) (Capon *et al* 1984). Mertensene (**97**) had previously been reported as the major metabolite of *P. mertensii*, collected at Cape Jervis in South Australia but had been assigned the wrong structure (Norton *et al* 1977). From a local species of *Plocamium*, collected along Cottesloe Beach near Perth, we isolated the known bromo analogue of **89**, bromoviolacene-1 (**98**) (Capon 1982) which is also present in a *Plocamium* sp from Big Rat Island together with plocamadiene-A (**88**) and the acyclic monoterpene (**99**) (Arrowsmith 1983).

A collection of *Phacelocarpus labillardieri* from Cosy Corner yielded (Capon *et al* 1988) compounds with structure similar to **100** and analogues reported from the same species collected in South Australia and Tasmania (Kauzlaskas *et al* 1982d).

A methanol extract of *Hypnea valentiae* collected at Quobba Lagoon produced pronounced muscle relaxation and hypothermia in mice and also blocked poly- and monosynaptic reflexes. The compound responsible for all these activities after purification was shown to be the unique iodinated nucleoside (**101**). A minor component of the extract was shown to be the isomer (**102**) which showed lower biological activity than (**101**) (Kauzlaskas *et al* 1983).

The only member of the family Bonnemaisoniaceae examined was a *Delisea* sp found near Hamelin Bay. The compounds obtained (**103-108**) had previously been isolated from *D. fimbriata* collected near Sydney (Capon 1982).

Marine Cyanophytes

Blue-green algal mats and stromatolites are the dominant autotrophs of the hypersaline waters of Shark Bay, Western Australia. Algal mats extend from shallow subtidal depths (*ca* 4 m) to an elevation of *ca* 2 m above low water level and can be differentiated into four basic types and three intergradational types that can be distinguished on the basis of surface texture and colour (Logan *et al* 1974). Each mat type is colonized by a dominant cyanophyte. Three of the seven types of algal mats (Table 4) were examined for the presence of lipophilic metabolites. Extraction of the freeze-dried algal mats with methylene chloride: methanol afforded, in all but one case, a white translucent polymer. Chemical studies showed it to be poly-β-hydroxybutyrate (PHB) (**109**) and either a heteropolymer containing units of β-hydroxybutyric and β-hydroxypentanoic acids (**110**) or an inseparable mixture of PHB and poly-β-hydroxypentanoate (PHV) (Capon *et al* 1983). A similar mixture was obtained from an *Aphanothece* sp from Lake Joondalup. The results obtained (Table 3) establish the presence of polyesters in cyanobacteria growing in vastly different environments, viz. a permanent freshwater lake and a variable hypersaline intertidal zone. It also seems clear that one of the polyesters is PHB, a chiral polymer which normally occurs as hydrophobic granules in the cells of a wide variety of bacteria. Only a few reports of its presence in cyanobacteria have appeared. The occurrence and identification of PHB in the blue-green alga, *Chlorogloea fritschii*, after growth in the presence of acetate has been reported (Carr 1966). No PHB could be detected after growth of *C. fritschii* on an autotrophic medium in the absence of acetate, or growth of *Anabaena variabilis* in the presence or absence of acetate. PHB has been detected also in an *Oscillatoria* sp (Moore 1981).

Table 4

Polyesters from Cyanobacteria

Locality	Form	Cyanophyte	Polymer yield (pentanoate-butanoate)
Lake Joonadalup Perth	metaphyton	*Aphanothece* sp.	0.2%* (2:1)
Hutchison Bay Shark Bay	pustular mat	*Microcoleus* sp.	0.02%† (n.d.)
Hamelin Pool Shark Bay	smooth mat	*Schizothrix calcicola* (C.Agardh)Gomont.§ *Symploca laete-viridis*, Gomont. *Scytonema* sp.	00.3%† (1:1)
Hamelin Pool Shark Bay	tufted mat	*Lyngbya aestuarii* Gomont. *Microcoleus chthonoplastes* Thur.	0.03%† (1:4)
Hamelin Pool	pustular mat	*Entophysalis deusta* Drouet and Daly	0

* Yield based on wet wt
† Yield based on freeze dried wt of algal mat
§ Dominant cyanophyte

PHB and PHV are being evaluated for industrial use. Both are aliphatic polyesters of high molecular weight and stereoregularity and as such are good sources of chiral monomers. They are biodegradable in soil, can be plasticized and take glass-fibre filling very well. Their production from bacterial sources does not appear to be competitive with oil-based thermoplastics yet. The occurrence of these polymers in cyanophytes, which are autotrophic, is of some significance. Large scale cultivation of the cyanophytes dominating the hypersaline environments of Shark Bay may allow the production of these polymers at competitive costs.

Sea Grasses

Amphibolis antarctica and *Posidonia australis* are the major sea grasses of Shark Bay, Western Australia (Walker *et al* 1988). Meadows of these grasses dominate the metahaline regions of the Bay establishing complex floral and faunal communities within monospecific stands of grass. The grasses are rarely directly grazed but form a detrital energy chain *via* the shedding and subsequent settling of leaves (Walker & McComb 1985). An ongoing study of the organic geochemistry of the sediments of Shark Bay required knowledge of the input of hydrocarbons from sea grass leaves. *Posidonia australis* had been examined in this context but no study existed for *A. antarctica* which provides the larger biomass of these sea grasses in Shark Bay (Walker *et al* 1988). Examination by GC/MS of the hydrocarbons from the leaves of *A. antarctica* showed the presence of *n*-alkanes (C_{17}-C_{25}, odd number predominance) and a diterpene hydrocarbon. Extraction of a large sample of leaves, followed by silicic acid and alumina chromatography of the crude extract, yielded a colourless oil, (0.0002% of fresh wt) to which structure (**111**) was assigned on the spectroscopic evidence (Dunlop 1985). Collections of *A. antarctica* from near Perth contained not only (**111**) but also the known diterpene hydrocarbons sandaracopimaradiene (**112**) and isopimaradiene (**113**).

Analysis of individual heads of leaves of *A. antarctica* from Shark Bay showed: (a) that *n*-alkanes are concentrated in juvenile leaves and diminish as the leaf ages; and (b) that (**111**), while not detected in juvenile leaves, increases with leaf age and persists in leaves which have become detritus. It is possible during high physical energy conditions, such as cyclones, that whole *Amphibolis* beds may be disturbed and, subsequently, buried thereby contributing both *n*-hydrocarbons and diterpenes to the sediment hydrocarbon profile. In samples from near Perth, the same distribution of *n*-alkanes and all three diterpenes is observed. Epiphytes on the leaves contribute a significant proportion of *n*-heptadecane.

Sediments

The physical and biological environments of Shark Bay have been the target of considerable studies (Logan & Cebulski 1970). A stable salinity gradient has been defined and this ranges from oceanic waters in the north, through a metahaline phase (Hopeless Reach and Freycinet Basin) to hypersaline water in Hamelin Bay. Associated with this there are three biotic communities with bivalves dominating the embayment plain of the oceanic environment with only sparse flora, sea grass cover in the metahaline and sparse algal flora and *Fragum* community in the hypersaline basins. The chemical assemblage of sediment hydrocarbons along the salinity gradient may be classified into two distinct chemogeographic types. Firstly, oceanic sediments contain *n*-alkanes and a suite of highly branched and branched/cyclic C_{25} alkenes. Hypersaline sediments are characterised by a high relative abundance of a $C_{25}H_{50}$ alkene (**114**) together with an analogous $C_{20}H_{40}$ alkene (**115**) and its parent $C_{20}H_{42}$ alkane (2,6,10-trimethyl-7-(3-methylbutyl)-dodecane) (**116**). A pair of alkanes $C_{21}H_{44}$ and $C_{22}H_{46}$ increase in concentration and relative abundance with depth. The hydrocarbons of the hypersaline basins are found in only trace amounts in oceanic sediments. These chemical signals are overlain by further input indicative of the immediate biotic community. The two chemically distinct regions are not aligned with the macrobiotic sea grass communities and the detailed hydrocarbon chemistry of the sea grass sediments indicates that the origin of the oceanic and hypersaline alkenes are derived from another undisclosed source (Dunlop & Jefferies 1985).

To the north of Shark Bay lies the land-locked marine sedimentary basin Lake McLeod. In the north-west of the basin, hypersaline ponds are maintained via the influx of marine waters through cavernous limestone and efflux away from the vents downslope to the east. Evaporation provides present day sequences of carbonate and gypsum (Logan 1987). During a preliminary examination of the organic geochemistry of these sequences, the compounds (**115**) and (**116**) were observed as major components of the carbonate mud hydrocarbons. At Cygnet Pond, a south to north transect from the pond to dry exposed shore demonstrated that the carbonate mud of the pond contained the alkene (**115**) while those of exposed carbonate contained the alkane (**116**). The presence of the alkene in pond sediment was not associated with macroscopic biota (*eg* the green algae *Cladophora* or the aquatic angiosperm *Ruppia* sp.). Likewise the alkane was not derived from cyanobacterial mats which cover the shore and are frequently buried (Dunlop unpublished results).

References

Arrowsmith N J 1983 An investigation of the metabolites from algae specimens of the Abrolhos islands, Honours Thesis, Department of Organic Chemistry, Univ W Aust 1-44.

Aso K 1939 Decomposition products of substances containing uronic acid III. Reductic acid, J Agr Chem Soc Japan 15:161-170.

Baker J T 1976 Some metabolites from Australian marine organisms. Pure & Appl Chem 48:35-44.

Bergquist P R 1978 Sponges. Hutchison & Co, London.

Bergquist P R & Wells R J 1983. Chemotaxonomy of the Porifera: The development and current status of the field. In: Marine Natural Products (ed P J Scheuer) Academic Press, New York, 5:1-50.

Bestow A W 1981 An investigation into the metabolites from *Plocamium mertensii* Honours Thesis, Department of Organic Chemistry, Univ W Aust 1-55.

Brennan M R & Erickson K L 1982 Austradiol acetate and austradiol diacetate, 4,6-dihydroxy-(+)-selinane derivatives from an Australian *Laurencia* sp. J Org Chem 47:3917-3921.

Cannon J R, Edmonds J S, Francesconi K A, Raston C L, Saunders J B, Skelton B W & White A H 1981 Isolation, crystal structure and synthesis of arsenobetaine, a constituent of the Western Rock Lobster, the Dusky Shark, and some samples of human urine. Aust J Chem 34:787-798.

Capon R J 1982 Marine natural products from the Porifera and Algae of the Western Australian coast. PhD Thesis, Department of Organic Chemistry, Univ W Aust 1-244.

Capon R J, Ghisalberti E L & Jefferies P R 1981a New sesquiterpenes from *Caulerpa flexilis* var *muelleri*. Aust J Chem 34:1775-1778.

Capon R J, Ghisalberti E L & Jefferies P R 1981b Isoprenoid dihydroquinones from a brown alga *Cystophora* sp. Phytochemistry 20:2598-2600.

Capon R, Ghisalberti E L, Jefferies P R, Skelton B W & White A H 1981c Structural studies of halogenated diphenyl ethers from a marine sponge. J Chem Soc Perkin Trans 1 2464-2467.

Capon R, Ghisalberti E L, Jefferies P R, Skelton B W & White A H 1981d Sesquiterpene metabolites from *Laurencia filiformis*. Tetrahedron 37:1613-1621.

Capon R J, Ghisalberti E L & Jefferies P R 1982a A new furanoterpene from a *Spongia* sp. Experientia 38:1444-1445.

Capon R J, Ghisalberti E L & Jefferies P R 1982b New tetrahydropyrans from a marine sponge. Tetrahedron 38:1699-1703.

Capon R J, Ghisalberti E L & Jefferies P R 1982c New aromatic sesquiterpenes from a *Halichondria* sp. Aust J Chem 35:2583-2587.

Capon R J, Ghisalberti E L & Jefferies PR 1983a Metabolites of the green algae, *Caulerpa* species. Phytochemistry 22:1465-1467.

Capon R J, Dunlop R W, Ghisalberti E L and Jefferies P R 1983b Poly-3-hydroxyalkanoates from marine and freshwater cyanobacteria. Phytochemistry 22:1181-1184.

Capon R J, Engelhardt L M, Ghisalberti E L, Jefferies P R, Patrick V A & White A H 1984 Structural studies of polyhalogenated monoterpenes from *Plocamium* species. 37:537-544.

Capon R J, Ghisalberti E L, Jefferies P R & Mori T A 1988 Sesquiterpenes from *Laurencia* spp. J Nat Prod 51:1302-1304.

Carr N G 1966 Occurrence of poly-βhydroxybutyrate in the blue-green alga, *Chloroglea fritschii*. Biochim Biophys Acta 120:308-310.

Cassidy M P 1982 Secondary metabolites from marine sponges Honours Thesis, Department of Organic Chemistry, Univ W Aust 1-70.

Cassidy M P, Ghisalberti E L, Jefferies P R, Skelton B W & White A H 1985 New tricyclic diterpenes from the sponge *Higginsia* sp. Aust J Chem 38:1187-1195.

Clayton M N 1981 Phaeophyta. In: Marine Botany. An Australasian Perspective (M N Clayton and R J King eds) Longman Cheshire, Melbourne, 105-137.

Dellar G, Djura P & Sargent M V 1981 Structure and synthesis of a new bromoindole from a marine sponge. J Chem Soc Perkin Trans 1 1680-1681.

Dunlop R W 1985 Diterpenoid hydrocarbons in the sea grass *Amphibolis antarctica*. Phytochemistry 24:977-979.

Dunlop R W, Ghisalberti E L & Jefferies P R 1989 Structure of a new dolastane diterpene from *Dictyota furcellata* (C.Ag.)J.Ag. Aust J Chem 42:315-319.

Dunlop R W, Jefferies P R 1985 Hydrocarbons of the hypersaline basins of Shark Bay, Western Australia. Org Geochem 8:313-320.

Edmonds J S & Francesconi K A 1981a The origin and chemical form of arsenic in the School Whiting. Marine Pollution Bulletin 12:92-96.

Edmonds J S & Francesconi K A 1981b Arseno-sugars from brown kelp (*Ecklonia radiata*) as intermediates in cycling of arsenic in a marine ecosystem. Nature 289:602-604.

Edmonds J S & Francesconi K A 1982 Isolation and crystal structure of an arsenic-containing sugar sulphate from the kidney of the Giant Clam, *Tridacna maxima*. X-ray crystal structure of (2*S*)-3-[5-deoxy-5-(dimethylarsinoyl)-β-D-ribofuranosyloxy]-2-hydroxypropyl hydrogen sulphate. J Chem Soc Perkin Trans 1 2989-2993.

Edmonds J S & Francesconi K A 1983 Arsenic-containing ribofuranosides: isolation from brown kelp *Ecklonia radiata* and nuclear magnetic resonance spectra. J Chem Soc Perkin Trans 1 2375-2382.

Francesconi K A 1980 Pigments of some echinoderms collected from Western Australian waters. Aust J Chem 33:2781-2784.

Francesconi K A 1983 Some aspects of the chemistry of marine natural products. MSc Thesis, Department of Organic Chemistry, Univ W Aust.

Grossert J S 1972 Natural Products from Echinoderms. Chem Soc Rev 1:1-26.

Kazlauskas R, Marwood J F, Murphy P T & Wells R J 1982a A blue pigment from a compound ascidian. Aust J Chem 35:215-217.

Kazlauskas R, Murphy P T & Wells R J 1982b Five new C_{26} tetracyclic terpenes from a sponge (*Lendenfeldia* sp). Aust J Chem 35:51-59.

Kazlauskas R, Murphy P T & Wells R J 1982c A brominated metabolite from the red alga *Vidalia spiralis*. Aust J Chem 35:219-220.

Kazlauskas R, Murphy P T, Wells R J & Blackman A J 1982d Macrocyclic enol-ethers containing an acetylenic group from the red alga *Phacelocarpus labillardieri*. Aust J Chem 35:113-120.

Kazlauskas R, Murphy P T, Wells R J, Baird-Lambert J A & Jamieson D D 1983 Halogenated pyrrolo[2,3-*d*]pyrimidine nucleosides from marine organisms. Aust J Chem 36:165-170.

Kraft G T & Woelkelring W J 1981 Rhodophyta-systematics and biology. In: Marine Botany. An Australasian Perspective (M N Clayton & R J King, eds) Longman Cheshire, Melbourne, 61-103.

Logan B W, Cebulski D 1970 Sedimentary Environments of Shark Bay, Western Australia. Amer Assoc Pet Geol Mem 13:38-84.

Logan B W 1987 The MacLeod Evaporite Basin, Western Australia: Holocene Environments, Sediments and Geological Evolution. Amer Assoc Petrol Geol Mem 44:1-135.

McRaild G N 1981 Chlorophyta. In: Marine Botany. An Australasian Perspective (eds M N Clayton & R J King). Longman Cheshire, Melbourne, 180-199.

Moore R E 1981 Constituents of Blue-Green Algae. In: Marine Natural Products (P J Scheuer, ed). Academic Press, London 1-52.

Norton R S, Warren R G & Wells R J 1977 Three new polyhalogenated monoterpenes from *Plocamium* species. Tetrahedron Letters 3905-3908.

Price I R 1981 Plants of the marine environment. In: Marine Botany An Australasian Perspective (eds M N Clayton & R J King). Longman Cheshire, Melbourne, 15-34.

Saito Y & Womersley H B S 1974 The Southern Australian species of *Laurencia* (Ceramiales: Rhodophyta). Aust J Bot 22:815-874.

Sims J J, Fenical W, Wing R M & Radlick P 1973 Marine Natural Products IV. Prepacifenol, a halogenated Epoxy sesquiterpene and precursor to pacifenol from the red alga, *Laurencia filiformis*. J Amer Chem Soc 95:972.

Spence I, Wells R J 1978 A novel pharmacological action by a terpene isolated from *Plocamium cartilagineum*. Roche Research Institute of Marine Pharmacology, First Research Rep 1:10.

Thompson J E, Walker R P, Wratten S J, Faulkner D J 1982 A chemical defence mechanism for the nudibranch *Cadlina luteomarginata*. Tetrahedron 38:1865-1873.

Walker D I & McComb A J 1985 Decomposition of leaves from *Amphibolis antarctica* (Labill) Sonder *et* Aschers, and *Posidonia australis* Hook. f. the major seagrass species of Shark Bay, Western Australia. Botanica Marina 28:407-413.

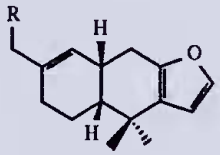
Walker D I, Kendrick G A & McComb A J 1988 The distribution of seagrass species in Shark Bay, Western Australia, with notes on their ecology. Aquatic Bot 30:305-317.

Wells, R J 1979 New metabolites from Australian marine species. Pure & Appl Chem 51:1829-1846.

APPENDIX Compounds isolated from Western Australian marine fauna and flora*

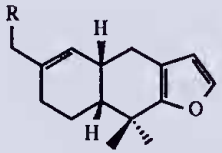
Porifera

Dysideidae



(1) R =H (0.13%) *Dysidea sp;Undet.genus*

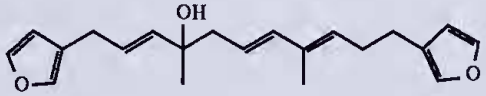
(2) R= SAc(0.005%) *Dysidea sp*



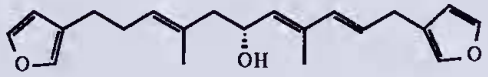
(3) R = H (0.13%) *Dysidea sp; Undet.genus*

(4) R = SAc(0.36%) *Dysidea sp*

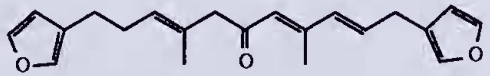
Spongiidae



(5) (1%) *Spongia sp*

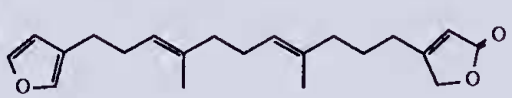


(6) (0.6%) *Leiosella sp*



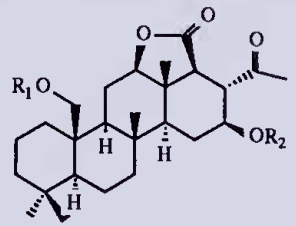
(7) (0.2%) *Leiosella sp*

*Porifera and Algae are listed according to families.For each compound a text number is given together with the source organism and,where available,yields expressed as percentage of the dry biomass.



(8) (1.35%) *Lendelfeldia sp*

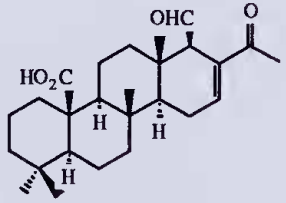
(9) (0.33%) *Lendelfeldia sp*



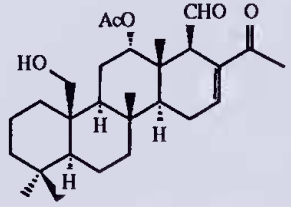
Lendelfeldia sp

(10) R_1 = Ac; R_2 = H

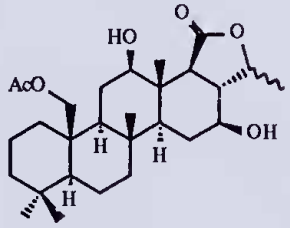
(11) R_1 = H ; R_2 = H



(12) *Lendenfeldia sp*

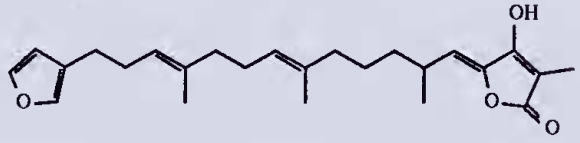


(13) *Lendefeldia sp*

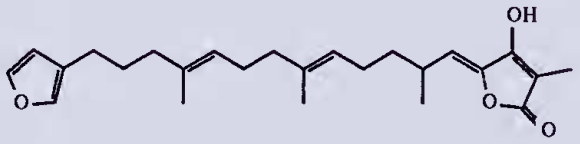


(14) *Lendefeldia sp*

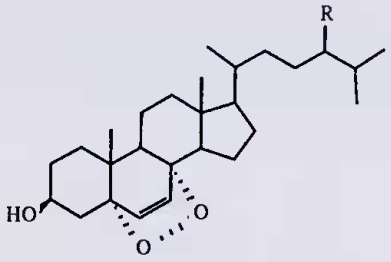
Thorectidae



(15) (0.02%) *Ircinia sp*



(16) (0.02%) *Ircinia sp*

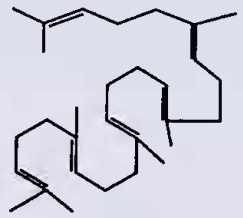


Ircinia sp

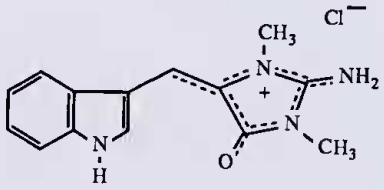
(17) R = H

(18) R = CH_3

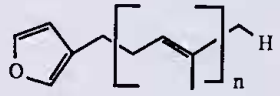
(19) R = CH_2CH_3



(20) (0.07%) *Ircinia sp*



(24) (0.2%) *Thorectandra sp*

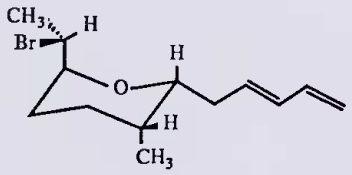


(21) n = 6 (0.12%) *Ircinia sp;* (0.2%) *Thorectandra sp* (0.2%)

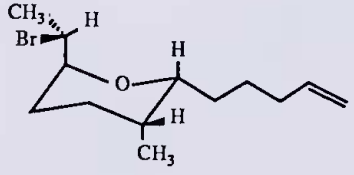
(22) n = 8 (0.2%) *Ircinia sp*

(23) n = 10 (0.08%) *Ircinia sp*

Haliclonidae

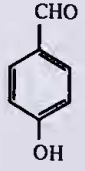


(25) (0.4%) *Haliclona sp*

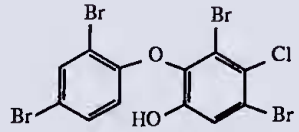


(26) (0.2%) *Haliclona sp*

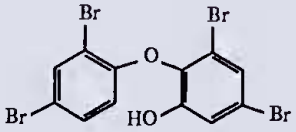
Callyspongidae



(27) (0.05%) *Dactylia sp*

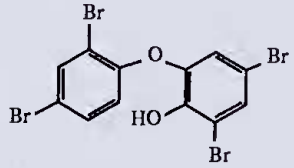


(28) (1.3%) *Undet.genus*



(29) (1.2%) *Undet.genus*

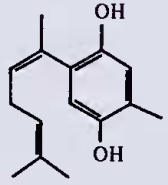
(2.0%) *New genus*



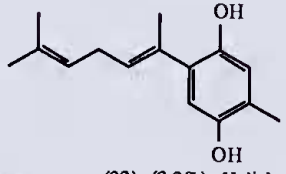
(30) (0.05%) *Undet.genus*

(0.05%) *New genus*

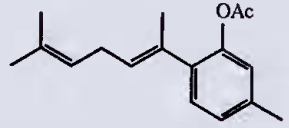
Halichondriidae



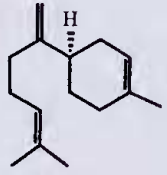
(31) (3.1%) *Halichondria sp*



(32) (3.2%) *Halichondria sp*

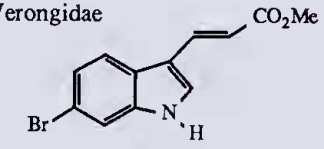


(33) (0.4%) *Halichondria sp*



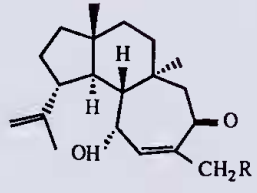
(34) (4.5%) *Halichondria sp*

Verongidae



(35) *Iotrochota sp*

Desmoxiidae

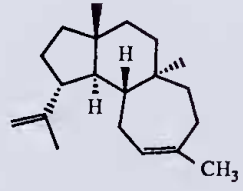


Higginsia sp

(36) R = CH_2OH

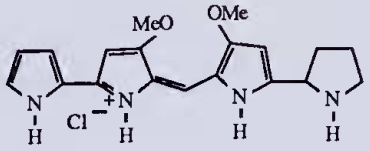
(37) R = CH_2OAc

(38) R = CH_3



(39) *Higginsia sp*

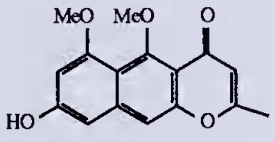
Compound Ascidian



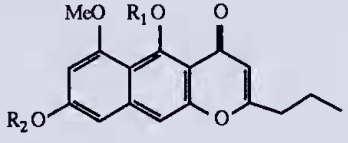
and (40)

Br⁻

Echinoderms

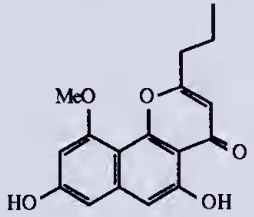


(41) *Comantheria solaris*

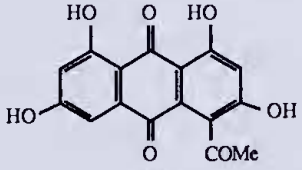


(42) R_1=Me, R_2=H *Comantheria solaris*

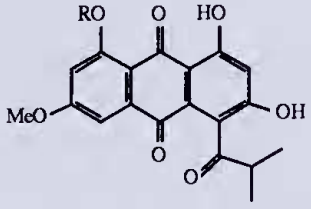
(43) R_1=R_2=H *Comantheria solaris*



(44) *Comantheria solaris*



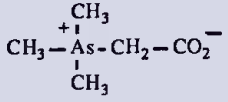
(45) *Coumatula solaris;*



(46) R = Me *Coumatula solaris; Comatula rotalaria*

(47) R = H *Comatula rotalaria*

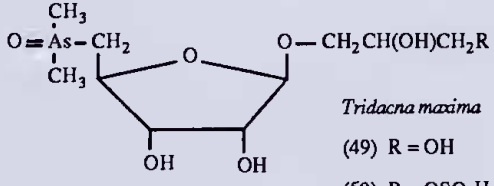
Others



(48) *Panulirus cygnus*

Carcharinus obscurus

Sillago bassensis



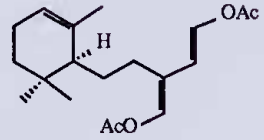
Tridacna maxima

(49) R = OH

(50) R = OSO_3H

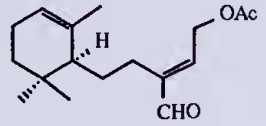
Algae

Caulerpaceae



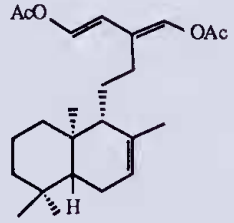
(51) (0.05%)

Caulerpa flexilis var muellerii

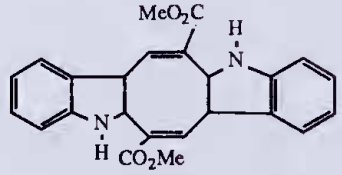


(52) (0.005%)

Caulerpa flexilis var muellerii



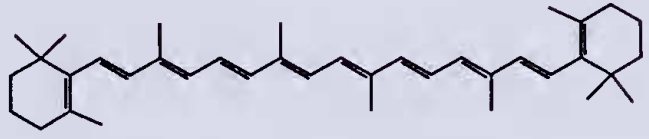
(53) (0.4%) *Caulerpa trifaria*



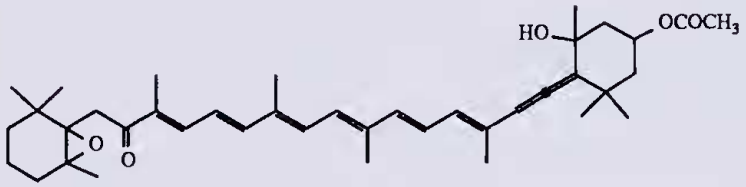
(54) (0.003%) *Caulerpa peltata*

(0.003%) *Caulerpa racemosa*

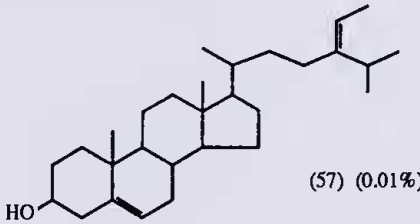
Cystoseiraceae



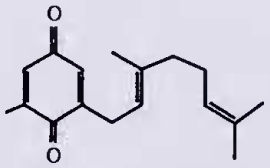
(55) (0.007%) *Cystophora sp*



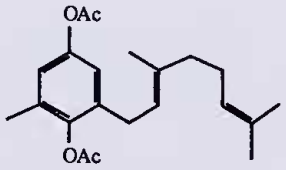
(56) (0.09%) *Cystophora sp*



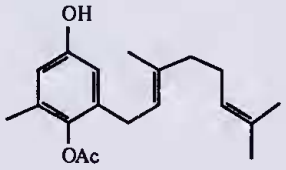
(57) (0.01%) *Cystophora sp*



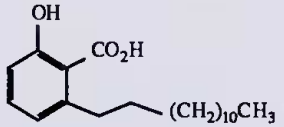
(58) (0.03%) *Cystophora sp*



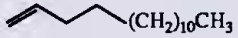
(59) (0.03%) *Cystophora sp*



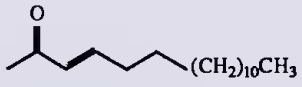
(60) (0.07%) *Cystophora sp*



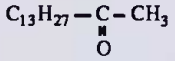
(61) (0.13%)
Caulocystis uvifera



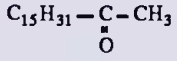
(62) (0.13%)
Caulocystis uvifera



(63) (0.04%)
Caulocystis uvifera

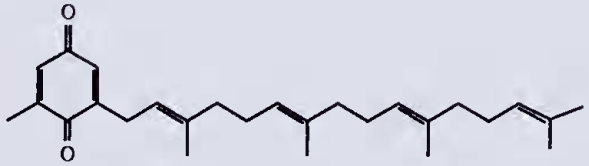


(64) (0.005%) *Caulocystis uvifera*

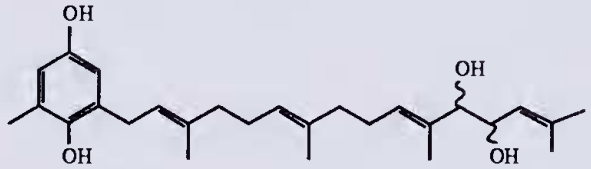


(65) (0.002%) *Caulocystis uvifera*

Sargassaceae

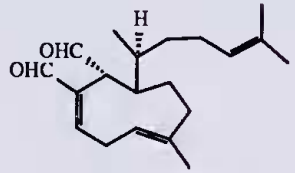


(66) (0.019%) *Sargassum sp*

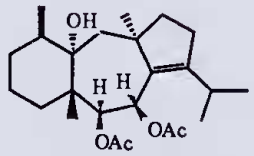


(67) (0.18%) *Sargassum sp*

Dictyotaceae

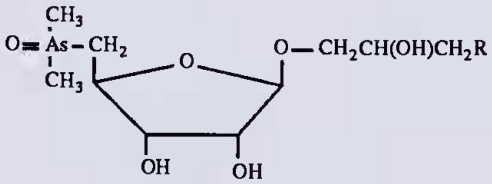


(68) (0.07%) *Glossophora sp*



(69) *Dictyota furcellata*

Alariaceae

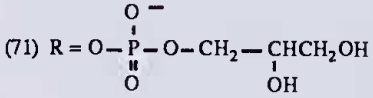


Ecklonia radiata

(49) R = OH

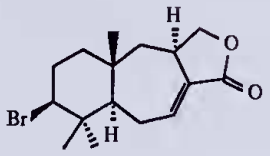
(50) R = OSO_3H

(70) R = SO_3H

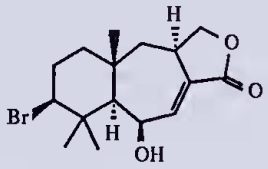


(71) R =

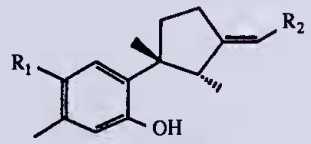
Rhodomelaceae



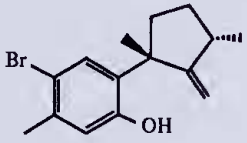
(72) (0.4%)
Laurencia filiformis f filiformis



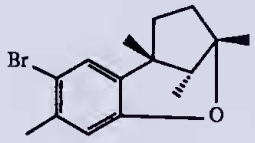
(73) (1.6%)
Laurencia filiformis f filiformis



Laurencia filiformis f heteroclada

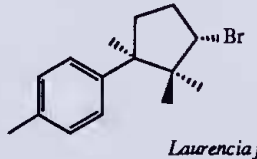


(77)
Laurencia filiformis f heteroclada

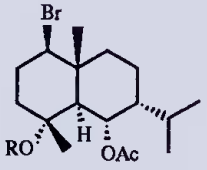


(78)
Laurencia filiformis f heteroclada

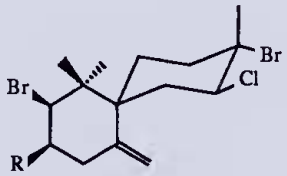
	R_1	R_2
(74)	Br	H
(75)	H	Br
(76)	Br	Br



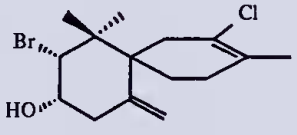
(79)
Laurencia filiformis f heteroclada



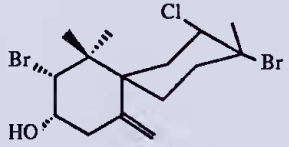
Laurencia filiformis
(80) R = H
(81) R = Ac



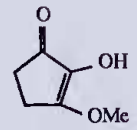
Laurencia majuscula
(82) (0.02%) R = H
(83) (1.2%) R = OH



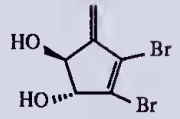
Laurencia majuscula
(84) (0.4%)



Laurencia majuscula
(85) (0.05%)

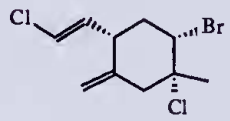


(86) (0.06%) *Chondria sp*

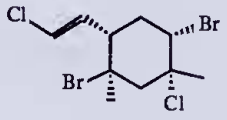


(87) *Vidalia spiralis*

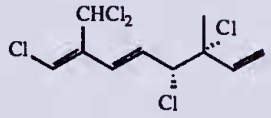
Plocamiaceae



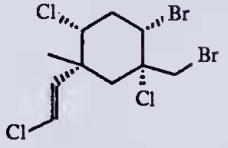
(88) (0.4%) *Plocamium mertensii*



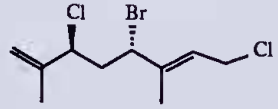
(89) (0.4%) *Plocamium mertensii*
Plocamium ssp



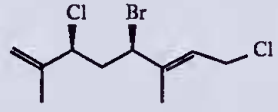
(90) (0.7%) *Plocamium mertensii*



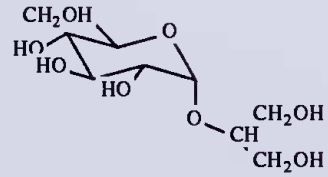
(91) (0.04%) *Plocamium mertensii*



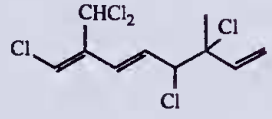
(92) (0.02%) *Plocamium mertensii*



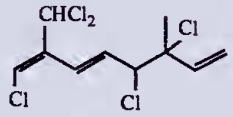
(93) (0.02%) *Plocamium mertensii*



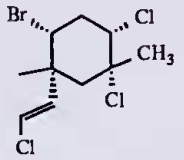
(94) (0.06%) *Plocamium mertensii*



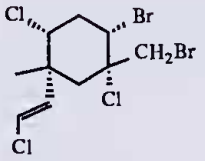
(95) *Plocamium preissianum*



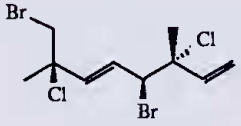
(96) *Plocamium preissianum*



(97) (0.05%) *Plocamium sp*

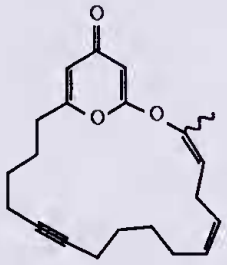


(98) *Plocamium sp*



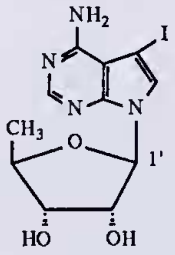
(99) *Plocamium sp*

Sphaerococcaceae



(100) *Phacelocarpus labillardieri*

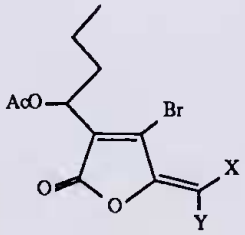
Hypneaceae



(101) 1' β-- Hypnea valendiae

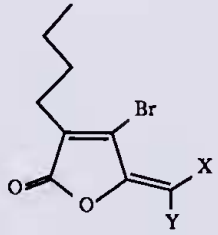
(102) 1' α--Hypnea valendiae

Bonnemaisoniaceae



Delisea sp

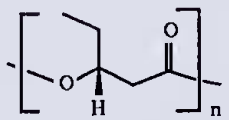
	X	Y
(103) (0.74%)	Br	H
(104) (0.74%)	H	Br
(105) (0.02%)	Br	Br



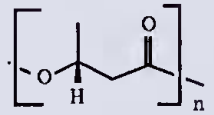
Delisea sp

	X	Y
(106) (0.06%)	Br	H
(107) (0.06%)	H	Br
(108) (0.10%)	Br	Br

Cyanophyta

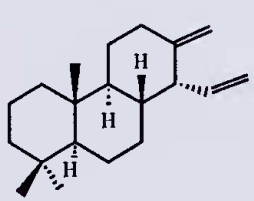


(109) blue-green algae

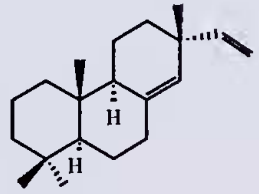


(110) blue-green algae

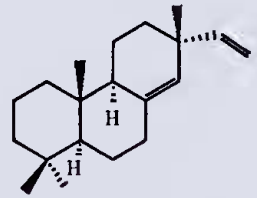
Seagrass



(111) *Amphibolis antarctica*

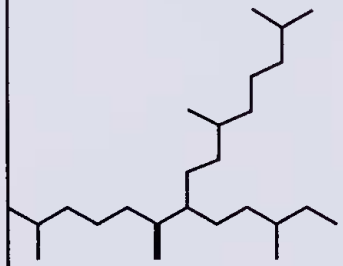


(112) *Amphibolis antarctica*

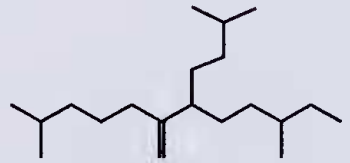


(113) *Amphibolis antarctica*

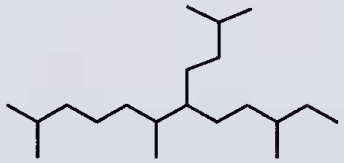
Sediment Hydrocarbons



(114)



(115)



(116)